

PATENT SPECIFICATION

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 (72) Inventors MANFRED HOPPE and ALBERT REICH



(54) PREPARATION OF GLYCIDE ETHERS

(71) We, INVENTA AG FÜR FORSCHUNG UND PATENT-
 VERWERTUNG, Zurich, A Body Corporate organised and existing under the
 laws of Switzerland, of Stempfenbachstrasse 38, Zurich, Switzerland, do hereby
 declare the invention, for which we pray that a patent may be granted to us and the
 method by which it is to be performed, to be particularly described in and by the
 following statement:—

The present invention relates to the preparation of glycidic ethers of mono- or
 polyhydroxy phenols.

It is known that commercially valuable, hardenable resins can be made by the
 action of alkali metal hydroxides on mixtures of epichlorhydrin and bis-(4-
 hydroxyphenyl)-propane ("bis-phenol A"). To prepare liquid diglycidic ethers of
 low molecular weight, 3—20 mols of epichlorhydrin are used per mol of phenolic
 groups and the excess epichlorhydrin is recovered after the reaction. A frequently
 used process is described in U.S. Patent Specification 2,841,595: 1.9 mols of 40%
 sodium hydroxide are added drop by drop to a mixture of epichlorhydrin and bis-
 phenol A in a molar ratio of 10:1 at 100°C over a period of 2 hours with
 simultaneous azeotropic separation of water. The excess epichlorhydrin is
 subsequently distilled off and the residue is taken up in an inert solvent. The
 solution so obtained is washed with water to remove the common salt formed, and
 then treated with excess sodium hydroxide solution to reduce the content of
 residual saponifiable chlorine (i.e. chlorine which can be split off).

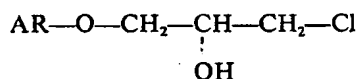
In the above process the high temperature of the reaction mixture during the
 azeotropic separation of water inevitably results in a very high loss of
 epichlorhydrin through alkaline decomposition. Commercial operation of the
 process is very protracted because of the azeotropic stage and the subsequently
 necessary separation of the common salt. Also, the process requires complicated
 equipment and controls and it involves a high consumption of energy.

Another process for making glycidic ethers of phenols is described in German
 Laid-open Patent specification No. 2,028,136. In this process a catalyst is used.
 The procedure is like that of U.S. Patent specification 2,841,595 with the sole
 difference that prior to the reaction with alkali, a catalyst is added and a partial or
 complete preliminary addition of the epichlorhydrin to the phenol molecule is
 effected by heating. After this, the alkali treatment is carried out, using a less than
 stoichiometric amount of alkali hydroxide solution, and azeotropic separation of
 water is carried out at the same time. As in the process of U.S. Patent specification
 2,841,595 the final stages of the process include distillation of epichlorhydrin,
 taking-up of the residue in solvent, washing of the solution with water to remove
 common salt, dehydrochlorination of the solution with excess alkali hydroxide
 solution and working up of the resin.

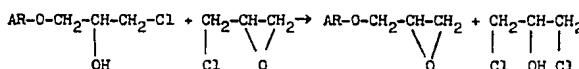
The principal object of the process described in the above mentioned German
 specification is to keep the loss of epichlorhydrin as low as possible and this is the
 purpose of the catalytic preliminary addition and the shortening of the azeotropic
 stage which is thereby possible. However in addition to the disadvantage of the
 process of U.S. Patent specification 2,841,595 there is now also the use of a
 relatively costly catalyst, which both increases manufacturing costs and causes an
 additional pollution of the waste water. Since it is still necessary to operate at
 relatively high temperatures during the first alkali treatment in order to achieve as
 complete a conversion as possible, the loss of epichlorhydrin through alkaline
 decomposition is still rather high.

A much simpler process than those described above is possible if, prior to the reaction with the alkali hydroxide, a substantially inert, at least partially water-soluble organic solvent is added to the epichlorhydrin/bis-phenol A solution. As a result of this solution-aiding addition, the contact between the organic phase and the aqueous alkali hydroxide phase becomes much better. Because of the greater reaction velocity, the etherification and dehydrochlorination reaction can take place at relatively low temperatures at which practically no epichlorhydrin is lost by alkaline decomposition. In contrast with the azeotropic processes, the separation of alkali chloride can be carried out simply and rapidly by allowing settling and separation of the aqueous phase.

A process of the above kind is described in Canadian Patent specification 658,455. In continuous operation, a total of 98—105% of the theoretical amount of alkali is caused to react in a number of steps. When less than the theoretically required amount of alkali liquor is used, complete etherification of the phenolic groups by epichlorhydrin is produced, but a proportion of the ether formed corresponds to the following general formula:



in which AR represent an aryl group. The relatively high proportion of saponifiable chlorine thereby obtained is, however, undesirable in epoxy resins. Furthermore, in the reaction of phenols with epichlorhydrin, an exchange of hydrogen chloride from the chlorhydrin ether present as intermediate product to the epichlorhydrin takes place as shown below with the formation of 1,3-dichloropropan-2-ol and is not reversible when a deficient amount of alkali is used.



Since a prerequisite of the economic production of glycidic ethers is the recycling of the epichlorhydrin used in excess, the transepoxydation reaction described above results in the recycled epichlorhydrin becoming enriched with dichloropropanol. The alkali hydroxide needed for re-converting the dichloropropanol into epichlorhydrin increases the amount of alkali required for forming glycidic ethers of low chlorine content.

In the process described in Canadian Patent specification 658,455 it is therefore possible to operate only with considerable excesses of alkali in order to obtain commercially usable products with a sufficiently low content of saponifiable chlorine. However, excess alkali in the presence of epichlorhydrin results in any case in the alkaline decomposition of the latter and, moreover, in an undesirable formation of chlorhydrin ethers and glycidic ethers with the alcohols used in this case. These by-products, because of their relatively high boiling points, are not completely separable from the resins formed and lead to a distinct reduction in heat stability in the polyaddition products which can be produced therefrom by hardening.

A similar process is described in Swiss Patent specification 411,362 and operated with *n*-butanol as an aid to solution. *n*-Butanol satisfies ideally the conditions which are required of such a reaction facilitating agent: low solubility in common salt solution, high water absorption and, thereby, good facilitation of solution between the alkali hydroxide solution and the organic phase. Using *n*-butanol, resins with low viscosities and a high epoxy group content can therefore be produced. Higher alcohols give only polyglycidic ethers with a lower epoxy group content and of high viscosity. In contrast to the use of lower and therefore more water-soluble alcohols, the loss of *n*-butanol through the separated common salt solution is extremely small.

In the above Swiss Patent specification, attention is drawn to the extremely small loss of epichlorhydrin. Practice shows, however, that in this process the loss of epichlorhydrin can be kept low only by use of approximately stoichiometric amounts of alkali hydroxide. In the recycling operation, however, these amounts of alkali are not sufficient to keep the content of easily saponifiable chlorine in the resin as low as is necessary for the majority of applications. For the preparation of commercially utilizable resins a relatively high excess of alkali hydroxide is

required and then, in the presence of the epichlorhydrin used in excess, this results in the described losses. Moreover, intermediate products of the saponification reaction, chiefly 1,2-epoxypropan-3-ol ("Glycidol"), accumulate in the epichlorhydrin/butanol circuit. Even in the lowest concentrations, glycidol results in residues with high viscosities and a turbidity which is hard to remove.

Additions of secondary alcohols have also been proposed in order to avoid the side reactions with the reaction aid. These alcohols are less easily etherified by epichlorhydrin. In the process described in German Patent specification 1,022,793 however, a high excess of alkali is still required for obtaining products of low chlorine content. The high excess of alkali results in the disadvantages that have already been mentioned.

Moreover, according to German Patent specification 1,022,793 with the use of aqueous alkali hydroxide solutions and subsequent settling and separation of the alkali chloride solution formed in the presence of secondary alcohols, it is only possible to obtain very highly viscous resins when unusually high excesses of epichlorhydrin are used. According to the German Patent specification in order to prepare resins having low viscosities, it is necessary to operate in anhydrous medium with solid alkali hydroxide. By this method, the commercially advantageous separation of the alkali salt formed as a solution is not possible and complicated working up becomes necessary.

According to the present invention glycide ethers are prepared by a process comprising so heating a mixture comprising a phenol, preferably polyhydric, an epihalohydrin, preferably epichlorohydrin, an aqueous alkali metal hydroxide solution and an at least partially water-miscible reaction aid, which is a substantially inert organic solvent, as to cause etherification and partial dehydrohalogenation, not more than 1 mol of alkali metal hydroxide being employed per equivalent of phenolic hydroxide groups, separating from the reaction mixture the salt solution formed preferably by allowing this solution to settle, distilling off excess epihalohydrin and the reaction aid from the reaction mixture, treating the remaining reaction product with an alkali metal hydroxide solution in excess with respect to the molar amount of halogen present in the remaining reaction product, thereby removing saponifiable halogen and forming an alkali metal salt solution, and separating off the alkali metal salt solution. The glycide ether solution produced by the process is preferably substantially neutralised, desirably to a pH of 5 to 6 and the glycide ether can then be isolated by conventional procedures e.g. filtration of the solution followed by distilling of the solvent(s).

The process according to the invention may be regarded as consisting of two stages, the first comprising the steps up to and including the distillation of excess epihalohydrin and the reaction aid from the reaction mixture and the second comprising the subsequent steps.

The equivalent ratio of the phenol to the epihalohydrin, i.e. ratio of phenolic hydroxyl groups to the epihalohydrin, is preferably at least 1:1.5, more preferably 1:3 to 1:7.

Sodium hydroxide is preferably employed as alkali metal hydroxide, preferably as an aqueous solution having a concentration of 5—70% by weight, more preferably 10—25% by weight. The alkali metal hydroxide solution is added to the reaction mixture in the first stage preferably in a number of portions, in particular two, the first portion being 2/3 and the second 1/3 parts by volume, and the reaction mixture is preferably stirred after all the solution has been added.

Alcohols, especially n-butanol, in concentrations of 10 to 200 per cent by weight, preferably 20—50% by weight referred to the amount of epihalohydrin employed, are preferably used as the at least partially water-miscible reaction aid. The amount of alkali metal hydroxide used in the first stage may be 0.6 to 1.0 mol per equivalent of phenolic hydroxyl groups, preferably 0.9 to 0.98 mol. The concentration of the aqueous solution is desirably so chosen that after the conversion of the alkali metal hydroxide good separation of the alkali metal salt solution formed from the organic phase is ensured. In the first stage, the reaction temperatures which are most advantageous for avoiding secondary reactions and for obtaining commercially favourable reaction velocities lie between 40 and 90°C preferably between 60 and 80°C.

In the second stage for removal of the residual saponifiable chlorine, desirably more than 0.02 equivalents of alkali metal hydroxide, preferably 0.1 to 0.25 equivalents, are employed in aqueous solution per equivalent of phenolic hydroxyl groups in the phenol originally employed, preferably in the presence of a solvent.

The concentration is again desirably so chosen that good separation of the alkaline common salt solutions is obtained. The same reaction temperatures as in the first are preferred for the second stage.

Depending of the viscosity to be expected for the end product, the use in the second stage of an inert organic solvent may be desirable. As inert solvents there may be used, for example, mixtures of xylene(s) with *n*-butanol or toluene with *n*-butanol.

The working-up of the epoxy compound is effected with advantage by azeotropic removal of water from the resin solution, filtering off of the precipitated residual common salt and subsequent removal of any solvent by distillation.

The process according to the invention is equally suitable for continuous and discontinuous operation. Whilst bis-(4-hydroxyphenyl)-propane is the preferred phenol any phenol may be used i.e. mono-, bi- and polynuclear phenols having one or more phenolic hydroxyl groups, such as hydroquinone, resorcinol, bis-(4-hydroxyphenyl)methane, bis-(4-hydroxyphenyl)diphenylsulphone, Novolak and resole resins, for example those which are prepared by acid or alkaline condensation of phenol with formaldehyde, etc.

The 1,3-dichloropropan-2-ol formed by transepoxydation does not in any way interfere with the re-use of excess epichlorhydrin and after a short time reaches a constant concentration in the epichlorhydrin/reaction aid circuit. The water entrained in the epichlorhydrin/reaction aid circuit and in the solvent top product of the second stage likewise does not interfere with their re-use.

In the process, a high selectivity of the alkali hydroxide used in the first stage is achieved, i.e. the consumption of epichlorhydrin through alkaline decomposition and through secondary reaction with the reaction aid is minimal. This is surprising and not predictable from the known processes since in all the latter, including multi-stage processes, rather high losses of epichlorhydrin arise. Thus, not only does the present process not need a catalyst but also it permits a considerable reduction in wastage of epichlorhydrin. Furthermore, the present process permits the elimination of operations that are costly in time and/or apparatus and that were necessary in prior processes: thus there is no need for azeotropic separation of water during the initial reaction with the alkali metal hydroxide and removal of the alkali metal halide formed can be achieved easily.

The yield and other characteristics features of a process according to the invention are compared in Table 1 with the best examples from German Laid-open Patent specification No. 2,028,136 the process of which may be regarded as a leading process according to the state of the art.

TABLE 1

	Results from Example 1 of the present invention	Comparison Examples from German Laid-open Patent specification 2 038 136	
		1	2
Yield of polyglycide (g./mol bis-phenol A) ether	338	337	337
Loss of epichlorhydrin (g./kg polyglycide ether)	27	70	45
Epoxy equivalent weight	188	184	189
Viscosity (poise at 25°C)	89	92	102
Readily saponifiable chlorine (% by weight)	0.01	0.45	0.49

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As a result of the small loss of epichlorhydrin, the absence of additional charging of the waste water with catalysts and their degradation products, the

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extremely low solubility of epichlorhydrin, reaction aid and solvent in the concentrated salt solutions and the low energy consumption, the present process is particularly satisfactory. The glycidic ethers of bis-(4-hydroxyphenyl)-propane obtainable by the present process are of above-average quality compared with those obtainable by known processes. They are distinguished by low viscosity, low content of readily saponifiable and unsaponifiable chlorine and negligible amounts of volatile components. The last property has the particular advantage that it permits the production of cross-linked products which are particularly heat-resistant. Plastics materials may be made from an ether made in accordance with the invention and a hardening agent.

The following Examples illustrate the present process.

Example 1.

228 parts by weight (1 mol) of bis-(4-hydroxyphenyl)propane were dissolved in 925 parts by weight (10 mols) of epichlorhydrin, 340 parts by weight of n-butanol and 60 parts by weight of water in a 2-litre multi-necked flask with a closable bottom outlet and equipped with an efficient stirrer, a thermometer, a heating device and a condenser, which can be changed over optionally to reflux or distillate removal, and the mixture was brought to 60°C. 242 parts by weight (1.33 mols) of 22% sodium hydroxide solution were then added dropwise continually over a period of 40 minutes with stirring and stirring was then continued for a further 10 minutes. During the dropwise addition, the temperature of the reaction mixture rose. By external cooling, the reaction mixture was kept at 70°C. After the stirrer had been turned off, the mixture immediately separated into two phases. The lower phase, a weakly alkaline common salt solution was drained off. The same process was thereafter repeated with another 104 parts by weight (0.57 mol) of the 22% alkali at 70°C. This time, a dropwise addition time of 10 minutes was used. After separation of the common salt solution formed, the organic phase was heated to 155°C at 50 Torr. In the process, 1132 parts by weight of an epichlorhydrin/butanol/water mixture distilled off. The resinous residue was dissolved, in the same apparatus, in 320 ml of a xylene/butanol mixture containing 80% by weight of xylene, 72.7 parts by weight (0.4 mol) of 22% sodium hydroxide solution were added and the mixture was stirred intensively for 30 minutes at 65°C. After the stirrer has been turned off, the alkaline common salt solution was separated off. The upper organic phase was neutralised by adding primary sodium phosphate and freed from water azeotropically by heating to 125°C at normal pressure. The anhydrous solution was then filtered to remove traces of common salt and the filtrate freed from the solvent by further heating to 160°C at 50 Torr. The residue was subjected to brief steam distillation in order to remove the last remains of solvent. By heating briefly under a vacuum of 50 Torr, a clear viscous resin having the following characteristics was obtained:

Viscosity at 25°C according to DIN 53015:	8900 cP
Epoxy equivalent weight according to DIN 16945:	188
Content of saponifiable chlorine:	0.01% by weight
Total chlorine content:	0.17% by weight
Gardner colour number:	2
Weight loss 3 hours at 140°C (DIN 16945):	0.26% by weight

Example 2.

The epichlorhydrin/butanol distillate from Example 1 was supplemented with 193 parts by weight of epichlorhydrin and reacted with bis-phenol A in the presence of alkali in the same way as is described in Example 1. The following characteristic values were obtained:

Viscosity at 25°C:	9200 cP
Epoxy equivalent:	189
Content of readily saponifiable chlorine:	0.01% by weight

Gardner colour number:

2

Weight loss 3 hours at 140°C:

0.18% by weight

Example 3.

216 parts by weight (2 mols) of *p*-cresol were dissolved in 925 parts by weight (10 mols) of epichlorhydrin 340 parts by weight of *n*-butanol and 60 parts by weight of water in the apparatus described in Example 1 and the mixture was heated to 60°C. 242 parts by weight (1.33 mols) of 22% sodium hydroxide solution were then added dropwise continually over a period of 40 minutes with stirring and stirring was then continued for a further 10 minutes. The temperature was kept at 70°C by slight cooling. After the stirrer had been turned off, the common salt solution formed was separated. 104 parts by weight (0.57 mol) of the same sodium hydroxide solution were then added, using a dropwise addition time of 10 minutes, stirring was continued for a further 10 minutes and the aqueous phase then separated. By heating to 140°C at 50 Torr, the epichlorhydrin/butanol/water mixture was distilled off. The residue was intimately mixed directly without solvent, in a period of 30 minutes at 80°C with 160 g (0.4 mol) of 10% sodium hydroxide solution, the alkali was separated after settling and the organic phase was neutralised with primary sodium hydrogen phosphate and heated to 120°C to remove dissolved water. The residue was subjected after filtration to a brief steam distillation in order to expel residual solvent and finally also freed from water by heating to 140°C at 50 Torr.

The *p*-cresyl glycid ether formed had the following characteristic values:

	Epoxy equivalent weight:	180	
	Content of saponifiable chlorine:	0.02% by weight	
25	Total chlorine content:	0.18% by weight	25
	Gardner colour number:	1—2	

WHAT WE CLAIM IS:—

1. A process for the preparation of glycid ethers comprising so heating a mixture comprising a phenol, an epichlorhydrin, an aqueous alkali metal hydroxide solution and an at least partially water-miscible reaction aid, which is a substantially inert organic solvent, as to cause etherification and partial dehydrohalogenation, not more than one mol of alkali metal hydroxide being employed per equivalent of phenolic hydroxide groups, separating from the reaction mixture the salt solution formed, distilling off excess epichlorhydrin and the reaction aid from the reaction mixture, treating the remaining reaction product with an alkali metal hydroxide solution in excess with respect to the molar amount of halogen present in the remaining reaction product, thereby removing saponifiable halogen and forming an alkali metal halide solution, and separating off the alkali metal halide solution.
2. A process according to claim 1 in which the ratio of phenolic hydroxyl groups to the epichlorhydrin is at least 1:1.5.
3. A process according to either preceding claim in which the reaction aid is an alcohol and is used in an amount of 10 to 200% by weight based on the weight of the epichlorhydrin.
4. A process according to claim 3 in which the amount of the alcohol employed is 20 to 50% by weight based on the weight of the epichlorhydrin.
5. A process according to any preceding claim in which the reaction aid is *n*-butanol.
6. A process according to any preceding claim in which the total amount of aqueous alkali metal hydroxide solution used in forming the mixture of this with the phenol, epichlorhydrin and reaction aid provides 0.6 to 1.00 equivalents of the hydroxide per equivalent of the phenolic hydroxyl groups.
7. A process according to any preceding claim in which the aqueous alkali metal hydroxide solution used for removing saponifiable halogen from the reaction product is employed in an amount of at least 0.02 equivalents of the hydroxide per equivalent of phenolic hydroxyl groups in the phenol originally employed.
8. A process according to any preceding claim in which the aqueous alkali

- metal hydroxide solution used is, in both cases, a 5 to 70% by weight aqueous sodium hydroxide solution.
- 5 9. A process according to any preceding claim in which the heating to effect etherification and partial dehydrohalogenation and the treatment whereby saponifiable halogen is removed are both carried out at a temperature in the range of 40 to 90°C. 5
- 10 10. A process according to any preceding claim in which the aqueous alkali metal hydroxide solution present in the mixture also comprising phenol, epihalohydrin and reaction aid is provided by addition of the hydroxide solution in a number of portions and the reaction mixture is stirred after all the solution had been added. 10
11. A process according to claim 10 in which two-thirds by volume of the hydroxide solution is added first and the remaining third by volume is added subsequently.
- 15 12. A process according to any preceding claim in which the phenol is polyhydric. 15
13. A process according to claim 12 in which the phenol is 2,2-bis-(4-hydroxy-phenyl)-propane.
- 20 14. A process according to claim 12 in which the phenol is bis-(4-hydroxy-phenyl)-methane. 20
15. A process according to any preceding claim in which the treatment to remove saponifiable halogen is carried out in the presence of an inert solvent or mixture thereof.
- 25 16. A process according to any preceding claim in which, after the alkali metal halide solution has been removed on the second occasion, the remaining reaction product is substantially neutralised and the glycidic ether isolated from it. 25
17. A process according to claim 1 substantially as hereinbefore described with reference to any of the Examples.
- 30 18. A glycidic ether made by a process according to any preceding claim. 30
19. A plastics material made from an ether according to claim 18 and a hardening agent.

For the Applicants,
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
53/64 Chancery Lane,
London, WC2A 1HN.